

# Recent Studies in Superconductivity at Extreme Pressures

James S. Schilling and James J. Hamlin

Department of Physics, Washington University  
CB 1105, One Brookings Dr, St. Louis, MO 63130, USA

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## Abstract

Studies of the effect of high pressure on superconductivity began in 1925 with the seminal work of Sizoo and Onnes on Sn to 0.03 GPa and have continued up to the present day to pressures in the 200 - 300 GPa range. Such enormous pressures cause profound changes in all condensed matter properties, including superconductivity. In high pressure experiments metallic elements,  $T_c$  values have been elevated to temperatures as high as 20 K for Y at 115 GPa and 25 K for Ca at 160 GPa. These pressures are sufficient to turn many insulators into metals and magnetics into superconductors. The changes will be particularly dramatic when the pressure is sufficient to break up one or more atomic shells. Recent results in superconductivity to Mbar pressures will be discussed which exemplify the progress made in this field over the past 82 years.

Superconductivity is a macroscopic quantum phenomenon which was discovered by G. J. Holst and H. K. Onnes [1] in Leiden in 1911, but not clearly understood until Bardeen, Cooper, and Schrieffer (BCS) [2] formulated their microscopic theory in 1957, exactly half a century ago. In the opinion of one of the present authors (JSS), had superconductivity not first been demonstrated in experiment, no theorist would have ever predicted it: who could imagine that two electrons, in spite of their Coulomb repulsion, might experience a net *attractive* interaction binding them together to form a bose particle? In a lecture in 1922 in honor of H. K. Onnes, Albert Einstein [3] considered various scenarios but finally conceded that the theory of superconductivity was in a sorry state with no end in sight. Three years later, and one year before his death, Kamerlingh Onnes wrote the following introductory paragraph in a paper of particular relevance to this conference [4]: “As no satisfactory theoretical explanation of the supraconductive state of metals has been given yet, which might serve as a guide for further investigations, it seems desirable to try, by changing the external conditions, to discover the factors which play a roll in the appearing of the phenomenon. These considerations led to the institution of an inquiry into the influence which elastic deformation exerts on the appearing of the supraconductive state. The results of this investigation are published here.” In this paper the authors go on to present the results of the first high-pressure experiments on any superconductor. Their results on Sn are reproduced in Fig. 1 where the superconducting transition temperature  $T_c$  of Sn is seen to decrease by 5 mK under a hydrostatic pressure of 300 bars. This paper is a model of careful experimentation and should be read by every student engaged in high pressure research, whatever the field of specialization.

The decrease in  $T_c$  with pressure for Sn and In is, in fact, found for all simple ( $s, p$ -electron) metal superconductors [5] and can be easily accounted for within BCS theory which is based on an electron-phonon pairing interaction:

$$T_c \approx \sqrt{\frac{\kappa}{m}} e^{-\kappa/\eta}, \quad (1)$$

where  $m$  is the cation mass,  $\kappa$  is the lattice spring constant, and  $\eta$  is the Hopfield parameter [6], a purely electronic term. In simple metals under pressure,  $\kappa$  increases much more rapidly than  $\eta$ , so that the exponential factor, and thus  $T_c$ , decreases rapidly. The decrease in  $T_c$  with pressure in  $\text{MgB}_2$ , which with  $T_c \simeq 40$  K possesses the highest value of  $T_c$  of any binary compound, can also be accounted for assuming electron-phonon interactions [7]. Note that if the isotopic mass  $m$  is varied in Eq. 1, instead of the pressure,  $T_c$  changes as  $T_c \sim m^{-1/2}$ , the classic isotope effect.

There are three primary ways in which high pressure experiments make important contributions to the field of superconductivity:

1. Test theories of superconductivity and reveal important systematics (see above)
2. Improve the properties of known superconductors

### 3. Create new superconductors

Besides testing theoretical models, high pressure experiments can also help improve the superconducting properties by showing the experimentalist how to push materials to higher values of  $T_c$ . This is of great technological relevance since no superconductor has yet been found which at ambient pressure possesses a transition temperature even half that of room temperature, in contrast to magnetic materials which order at much higher temperatures and have had an enormous commercial impact. For this reason the pressure dependence of  $T_c$  is often one of the first experiments to be carried out after a new superconductor is discovered: a large value of  $dT_c/dP$ , either positive or negative, implies the material is likely capable of higher transition temperatures at ambient pressure either through selective doping or positive or negative chemical pressure. This strategy was applied by Paul Chu's group with great success in the late 1980's. They determined that the transition temperature of the oxide cuprate La-Ba-Cu-O increased from 32 K to 40 K under only 1.4 GPa pressure [8]; the replacement of the large La cation with the smaller Y generated chemical pressure and resulted in the discovery of the first superconductor Y-Ba-Cu-O with a transition temperature ( $T_c \simeq 92$  K) above the boiling point of liquid nitrogen [9]. Several years later, in a collaboration with members of the Carnegie Institute of Washington, Chu's group was able to push the transition temperature of the mercury compound Hg-1223 to the record-high value  $T_c \approx 160$  K [10]. These are excellent examples of how high pressures can be used to improve the properties of superconducting materials which exemplify the philosophy and tradition of the group of Bernd Matthias at the University of California, San Diego which has been ably carried forth by many of his students, including Paul Chu and Matthias' successor, Brian Maple.

High pressures can also be used to synthesize new superconductors; simultaneous high temperature may be necessary [11], but sometimes not. In Fig. 2 is an updated and expanded version of the Periodic Table of Superconductivity originally drawn up by Bernd Matthias. There are altogether 52 elemental superconductors, 22 of which are only known to superconduct if sufficient pressure is applied. Of these 22, fully 12 were discovered by Jörg Wittig, a student of Werner Buckel at the University of Karlsruhe, Germany. Across the periodic table values of  $T_c$  range from 0.325 mK for Rh [12] or 0.4 mK for Li [13] (at 1 bar) to 20 K for Y (at 115 GPa) [14] or 25 K for Ca (at 160 GPa) [15]. This record high value of  $T_c$  for Ca was discovered by the group of Katsuya Shimizu, a student, and the successor, of Katsuya Amaya at the University of Osaka, Japan. Pressure-induced superconductivity is of great interest from a basic physics point of view since in a single high pressure experiment both the birth and the demise of the superconducting state can be witnessed. After a brief discussion of relevant high-pressure technology, we will examine several classes of pressure-induced transitions from the normal to the superconducting state.

High pressure technology has come a long way since the experiments of Sizoo and Onnes in 1925 on Sn and In at 300 bar pressure [4]. In the early 1970's Webb, Gubser,

and Towle developed a diamond-anvil cell (DAC) mated to the mixing chamber of a dilution refrigerator with a SQUID pickup coil capable of detecting minute magnetic flux changes [16]. With this beautiful device they tracked the decreasing  $T_c$  of Al metal from 1.17 K to 80 mK at 6.1 GPa [17]. Using this DAC as a model, one of the present authors (JSS) constructed a DAC suitable for higher pressures where superfluid He was loaded into the gasket hole to serve as pressure medium [18]. The opposing diamond anvils were then pushed into the gasket at 2 K using a He-gas driven double membrane. Thus far pressures as high as 220 GPa have been generated in this DAC at cryogenic temperatures, if no pressure medium is used. Magnetic flux changes are detected by one of two matched counterwound pickup coils connected either to a lock-in amplifier or a DC SQUID. Shimizu *et al.* [19] utilize a DAC designed to generate Mbar pressures at temperatures as low as 5 mK; this DAC made possible the discovery of pressure-induced superconductivity in O<sub>2</sub> near 100 GPa [20].

An enhancement in the detection limit for superconductivity is provided by the double modulation technique utilized by Timofeev *et al.* [21] at the Carnegie Institute in Washington. Vohra and Weir have developed so-called designer diamond anvils where up to 8 electrical leads or pickup loops are grown into the diamond anvil itself [22]. These anvils offer great promise for future quantitative electrical resistivity or ac susceptibility measurements in the multi-Mbar pressure range.

Let us now return to the Periodic Table of Superconductivity in Fig. 2. An examination of the maximum measured values of  $T_c$  at ambient or high pressure reveals that the lighter elements tend to do better. This is particularly evident for the alkaline earths going from Ba (5 K) to Sr (7 K) to Ca (25 K) and for the alkali metals from Cs (1.3 K) to Li (14 K). The lightest element, of course, is hydrogen. Many years ago Ashcroft [23] predicted that superconductivity near room temperature might be in the offing if only enough pressure is applied to make it metallic. Alas, the metallic state in hydrogen has not yet been sighted, except at very high temperatures (3000 K) [24] where superconductivity has little chance. Should metallic hydrogen prove to be fluid at low temperatures, then two-component superconductivity from the electrons and protons has been predicted with a myriad of fascinating ground states both with and without an applied magnetic field [25]. Is it realistic to hope that metallic hydrogen will be fluid at low temperatures in some pressure range? A hint at an answer is given by the fact that the melting curve of Na drops precipitously from 1000 K at 30 GPa to 300 K at 118 GPa [26], a significantly lower melting temperature than at ambient pressure!

As seen in Fig. 2, the Periodic Table of Superconductivity contains four classes of elemental solids that refuse to superconduct at ambient pressure: (i) the non-metals like H<sub>2</sub>, O<sub>2</sub>, Si, or Ge, (ii) elements like Fe, Co, Ni, Mn, as well as most rare earths and many actinides which are magnetic, the arch-enemy of superconductivity, (iii) the early, trivalent *d*-electron elements Sc, Y, and Lu, and (iv) the monovalent alkali and noble metals, excepting Li which barely makes it with  $T_c \simeq 0.4$  mK. The first class is the easiest to understand: without conduction electrons, superconductivity

doesn't have a chance. How does one predict what pressure is necessary to turn an insulator into a metal? With ample financial resources one can carry out a full scale electronic structure calculation or, as a cost-saving alternative, one can use the simple Goldhammer-Herzfeld criterion [27] for metallization which states that a given substance should be metallic if the ratio of its molar refractivity to its molar volume is equal to or greater than 1, i.e.  $R/V \geq 1$ . Using the equation of state, it is thus trivial to estimate the metallization pressure if the initial value of  $R/V$  is known (the change in  $R$  with pressure can be neglected).  $R$  is obtained from the measured atomic polarizability  $\alpha$ , where  $R = (4\pi\alpha/3)N_A$  and  $N_A$  is Avagadro's number. In Fig. 3 the ratio  $R/V$  is plotted for all elements (upper figure) [28] and compared to the actual electronic state of all elemental solids (lower figure). The Goldhammer-Herzfeld criterion is seen to have an amazing predictive power.

The fact that diamond anvils are transparent to visible light allows optical transmission and absorption experiments in a DAC to determine the band gap  $E_g$  of an insulating material as a function of pressure. If white light is used, the light transmitted through the sample will appear yellow, orange, or black if  $E_g \approx 2.2$ , 1.7, or 1.4 eV, respectively. Ashcroft [29] has recently pointed out that in hydrogen-rich compounds, such as  $\text{LiBH}_4$  and  $\text{LiAlH}_4$ , the hydrogen may be subjected to lattice pressure which could significantly reduce the external pressure required for metallization. In Fig. 4 microscopic photographs of the light transmitted through the two insulating compounds  $\text{LiBH}_4$  and  $\text{LiAlH}_4$  are shown for a sequence of increasing pressures to  $\sim 50$  GPa. In  $\text{LiBH}_4$  no coloration of the white light is seen to 53 GPa, indicating that the band gap remains greater than 2.2 eV throughout the experiment. In contrast, in  $\text{LiAlH}_4$  the transmitted light begins to change color at 30.8 GPa, becoming progressively more red to 42 GPa; however, further loading to 75 GPa resulted in no further change in color. The fact that upon unloading the color change is not reversible gives evidence for an irreversible phase transition.

The second class of elemental solids that do not superconduct at ambient pressure are those which are magnetic: the 3d transition metals, the rare earths (4f), and the actinides (5f). This is a vast playground for high pressure research where the possibilities include both transitions from one form of magnetism to another as well as from magnetism to superconductivity [18]. For example, Shimizu *et al.* [19, 30] have shown that Fe loses its ferromagnetism when it transforms from the bcc to the hcp  $\epsilon$ -phase near 14 GPa, allowing superconductivity to appear with  $T_c$  reaching a maximum value of 2.1 K at 21 GPa. For lack of space we will not discuss pressure-induced transitions in magnetic substances further.

The third class of non-superconducting elemental solids are the early, trivalent  $d$ -electron elements Sc, Y, and Lu. Why is superconductivity lacking here? The simple answer is that they don't have a sufficient number of  $d$  electrons in the conduction band. The more  $d$  electrons a given conduction band has, the higher the density of states and the more likely it is to support superconductivity. Superconductivity in Sc [31], Y [32], and Lu [33] was discovered in high pressure experiments by Wittig

and coworkers. This is not surprising since it is well known that the application of pressure increases the number of  $d$  electrons in a band. This  $s-d$  transfer is expected on very general grounds [34]: the kinetic energy  $\sim V^{-2/3}$  increases much faster under pressure than the potential energy  $\sim V^{-1/3}$ ; since  $s$ -orbitals possess more radial nodes (higher kinetic energy) than  $d$ -orbitals, they shift to higher energy much faster under pressure, thus causing  $s$  electrons to be dumped into the  $d$  band. Hamlin *et al.* have recently taken Y, Sc, and Lu to pressures as high as 115 [14], 74 [35], and 174 GPa [36], respectively, and found that  $T_c$  increases to temperatures as high as 20 K, as seen in Fig. 5. The upward curvature in  $T_c(P)$  for Sc suggests that extending the experiments into the Mbar pressure range may result in a significant enhancement in  $T_c$ . Such experiments on Sc are currently underway.

One nagging question remains: why is the early, trivalent  $d$ -electron metal La superconducting at ambient pressure, but Sc, Y, and Lu are not? We will return to this question after considering the alkali metals.

Superconductivity in the alkali metals has recently been reviewed by one of the present authors (JSS) [37]. The first alkali metal to exhibit superconductivity was discovered by Wittig [32] in 1970 for Cs at 1.3 K under 12 GPa pressure. Electronic structure calculations [38] reveal that appreciable  $s-d$  transfer ( $6s$  to  $5d$ ) occurs in this pressure range, i.e. Cs becomes a transition metal. The appearance of superconductivity is thus not surprising. However, if pressure-induced  $s-d$  transfer is responsible for the superconductivity of Sc, Y, Lu, and now Cs, how can it be that Li, where  $s-d$  transfer plays no role, becomes superconducting under pressure at relatively high temperatures (14 K)? The alkali metals are believed to be model free electron systems with nearly spherical Fermi surfaces. The particularly low electronic density of states of monovalent free-electron systems, the alkali and noble metals, contributes strongly to the lack of superconductivity at ambient pressure, with the exception of Li where  $T_c$  lies at extremely low temperatures (0.4 mK). In  $s,p$ -electron system, like Pb, Sn, In, or Zn, which manage to become superconducting at ambient pressure,  $T_c$  invariably *decreases* under pressure, as pointed out above. It would, therefore, appear highly unlikely that pressure would induce superconductivity in Li, Na or the noble metals where  $s-d$  transfer is relatively unimportant.

The resolution of this apparent paradox was given by Neaton and Ashcroft who calculated the electronic properties of Li [39] and Na [40] at Mbar pressures and obtained for Li the remarkable  $2s$ -electron density shown in Fig. 6. Not only is a clear tendency evident that the Li cations pair up, but the  $2s$  electrons are seen to be concentrated in interstitial regions rather than between the paired Li cations. The electronic properties they obtain at Mbar pressures are highly anomalous, the conduction bandwidth even *narrowing* under compression, a highly counterintuitive result in direct opposition to standard textbook dogma. The electron-phonon interaction also increases strongly. The physical picture they offer can be illustrated using Fig. 7 which depicts the ion cores as well separated at ambient pressure but beginning to touch at Mbar pressures. Since the conduction electrons must avoid the cation

core region because of Pauli principle and orthogonality constraints, the free volume available to them outside the ion cores becomes quite small under Mbar pressures, forcing these electrons into the interstitial sites and away from the regions between the cation cores. The low symmetry of the interstitial sites forces the conduction electrons to take on higher angular momentum character, i.e. for  $s$  electrons more  $p$  or  $d$  character, thus improving the likelihood that superconductivity occurs. This picture is not restricted to the alkali metals, but is quite general [40] and also applicable to the transition metals, as we discuss below. In Li and Na, therefore, one may speak of significant pressure-induced  $s - p$  rather than  $s - d$  transfer.

In a very recent paper Feng *et al.* [41] pose the interesting question whether the anomalous properties predicted and found for Li and Ca under pressure carry over to  $\text{CaLi}_2$ , the only known binary compound containing these two elements. Detailed calculations by these authors lead them to predict that “the elevated density of states at the Fermi level, coupled with the expected high dynamical scale of Li as well as the possibility of favorable interlayer phonons, points to potential superconductivity of  $\text{CaLi}_2$  under pressure”. We have carried out a search for superconductivity in  $\text{CaLi}_2$  both at ambient pressure, where no superconductivity was found above 1.10 K, and high pressure [42]. The results of the latter electrical resistivity experiments are shown in Fig. 8 where a superconducting transition is seen to appear below 2 K at 11 GPa. With a further increase in pressure,  $T_c$  increases and passes through a maximum at 13 K near 40 GPa.

The physical picture in Fig. 7, that the free volume available to the conduction electrons is sharply reduced as pressure brings the ion cores together, can also be applied to the early, trivalent  $d$ -electron metals Sc, Y, La, and Lu. This was first pointed out by Johansson and Rosengren [43] who were able to analyze  $T_c(P)$  data for La and La-Y alloys in terms of the reduction in the free volume available to the conduction electrons as pressure is applied. They used the ratio  $r_a/r_c$  of the Wigner-Seitz radius to that of the cation core as a measure of this free volume. In Fig. 9 we plot  $T_c$  versus ratio  $r_a/r_c$  for Sc, Y, La, and Lu, where we neglect any change in  $r_c$  with pressure compared to that in  $r_a$ , where  $r_a \propto V^{1/3}$ . For superconductivity to set in under pressure, evidently the ratio  $r_a/r_c$  must decrease to the value 2.2 or smaller. The vertical arrows mark the value of  $r_a/r_c$  for each elemental metal at ambient pressure. Note that for these four elemental metals the ambient pressure value of  $r_a/r_c$  is smallest for La which is consistent with the fact that La is already superconducting at ambient pressure, but Sc, Y, and Lu are not.

The alkali metals are also included in Fig. 9. Li is seen to fit in quite well with the trivalent  $d$ -electron systems. However K, Rb, and Cs’s ambient pressure value of  $r_a/r_c$  would lead to the expectation that they would superconduct at ambient pressure, which they don’t. Perhaps our neglect of any change in the core radius  $r_c$  with pressure is oversimplified, as is our attempt to compare the properties of monovalent and trivalent elemental solids.

If the electronic properties of conduction electrons in a solid become highly anoma-

lous as the ion cores approach each other under very high pressure, how much greater the changes would be if sufficient pressure is applied to actually begin to break open the individual atomic shells inside the ion core! As each atomic shell is broken open and its electrons dumped into the conduction band, all solid state electronic properties would fluctuate wildly. Things finally settle down when at astronomic pressures all shells have been broken open and we have a structureless Thomas-Fermi electron gas. Here it would seem likely that superconductivity and magnetism would weaken and ultimately disappear. This progression of events is mirrored schematically in the changes in the superconducting transition temperature shown in Fig. 10 where  $T_c$  is seen to fluctuate strongly with pressure. In our experiments to only a few Mbars we are only probing a relatively modest fraction of this mountain range. Science at high pressures has an exciting future to look forward to!

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- [6] Note that  $\eta \equiv N(E_f) \langle I^2 \rangle$ , where  $N(E_f)$  is the electronic density of states and  $\langle I^2 \rangle$  the mean-square electron-phonon matrix element; see: Hopfield J J 1971 *Physica (Amsterdam)* **55** 41
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# Figure Captions

**Fig. 1.** Electrical resistance versus temperature (units of  $^4\text{He}$  vapor pressure) under hydrostatic pressures of 4, 95, 193, and 300 bar from Ref. [4].  $T_c$  decreases under pressure. Figure reproduced with permission from the Kamerlingh Onnes Laboratory, Leiden, The Netherlands.

**Fig. 2.** Periodic Table of Superconductivity listing 30 elements which superconduct at ambient pressure (yellow) and 22 elements which only superconduct under high pressure (green, bold black frame). For each element the upper position gives the value of  $T_c(\text{K})$  at ambient pressure; middle position gives maximum value  $T_c^{\text{max}}(\text{K})$  in a high-pressure experiment at  $P(\text{GPa})$  (lower position).  $T_c$  values from Refs. [5, 13].

**Fig. 3.** (upper) Ratio of atomic molar refractivity versus molar volume  $R/V$  for elemental solids from Ref. [28]. (lower) Corresponding periodic table where metals, semimetals/semiconductors, and insulators are color coded.

**Fig. 4.** Transmitted light micro-photographs of  $\text{LiBH}_4$  and  $\text{LiAlH}_4$  at ambient temperature to 53 and 42 GPa, respectively. Sample diameter is  $\sim 100 \mu\text{m}$ . Color gives estimate of band gap:  $E_g \approx 2.2 \text{ eV}$  (yellow),  $1.7 \text{ eV}$  (orange),  $1.4 \text{ eV}$  (black).

**Fig. 5.** Superconducting transition temperature versus pressure for Sc [35], Y [14], and Lu [36].

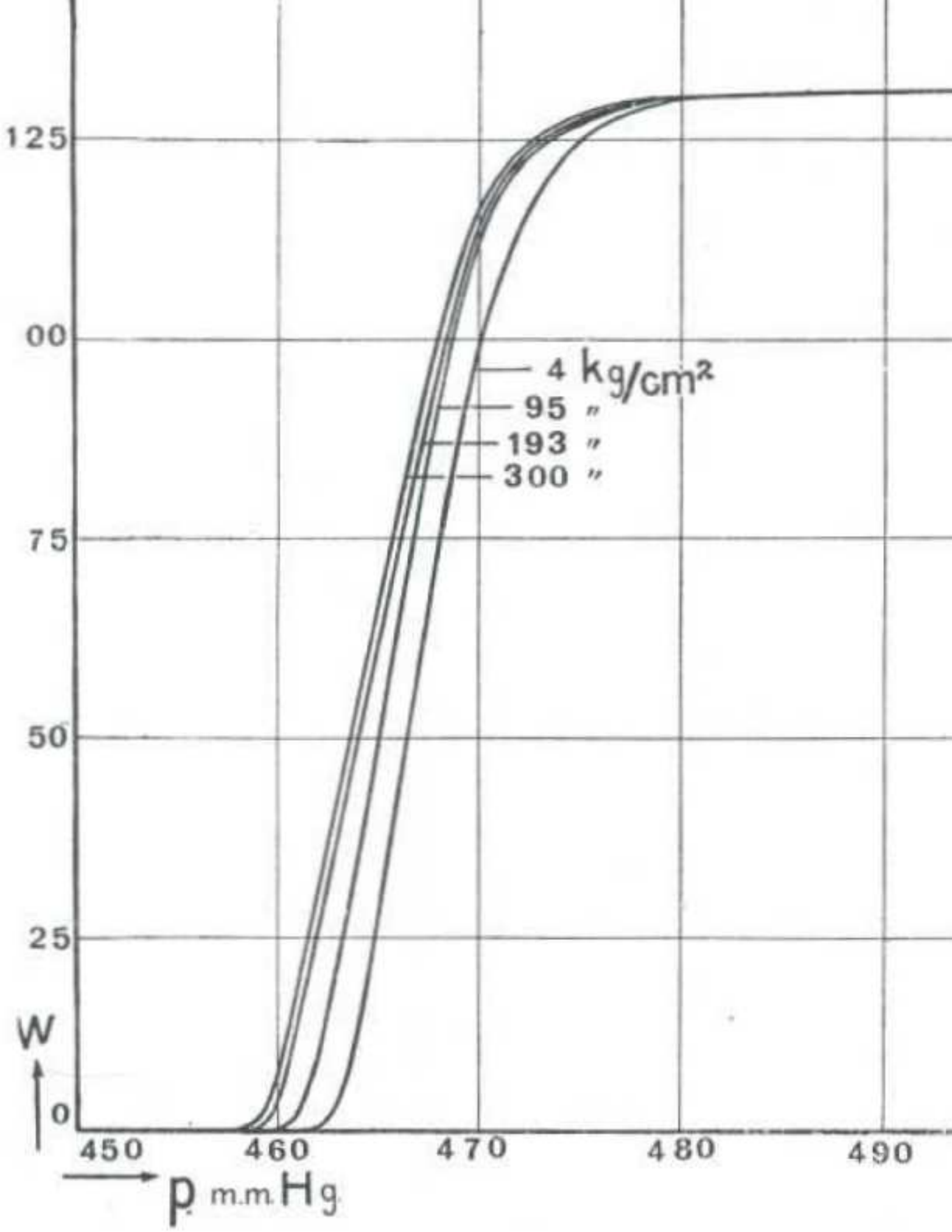
**Fig. 6.** Relative charge density of Li's  $2s$  conduction electrons at 100 GPa pressure. The  $\text{Li}^{1+}$  ions are centered in the red regions. Reprinted by permission from Macmillan Publishers Ltd: [NATURE] Neaton J B and Ashcroft N W 1999 *Nature* **400** 1141, copyright (1999).

**Fig. 7.** Schematic representation of cation electron cores at (left) ambient pressure and (right) extreme pressure.  $r_c$  and  $r_a$  define the core and Wigner-Seitz radii, respectively.

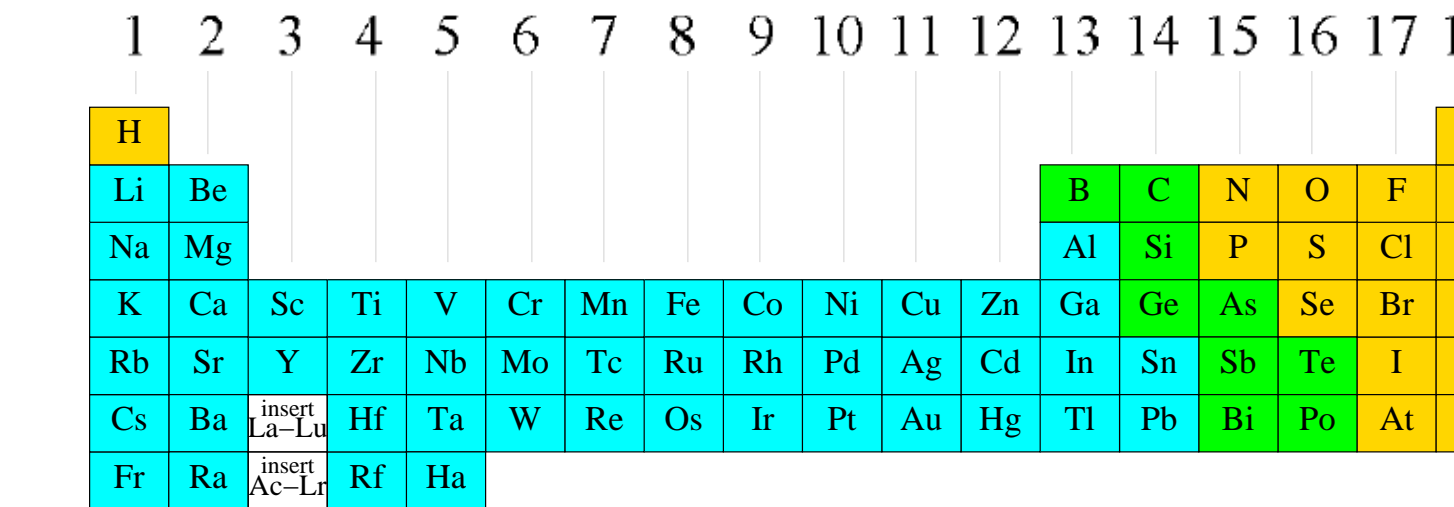
**Fig. 8.** Resistance versus temperature for annealed  $\text{CaLi}_2$  at 13.4, 20, 22, and 24 GPa. Inset gives expanded view of superconducting transition at 24 GPa for dc magnetic fields of 500 Oe (2 runs) and 0 Oe (3 runs), where colors distinguish runs.

**Fig. 9.** Pressure-induced superconducting transition temperature versus ratio  $r_a/r_c$  for the trivalent  $d$ -electron metals Sc, Y, La, Lu and the alkali metals Li and Cs. Vertical arrows mark values of  $r_a/r_c$  at ambient pressure.

**Fig. 10.** Schematic representation of the superconducting transition temperature versus (astronomic) pressures showing the drastic changes which occur when the atomic shell structure is progressively broken up.



Fr	Ra

# Transmitted Light Photographs

